DEVELOPMENT OF NATURAL ADHESIVE USING LIGNIN AND SOY PROTEIN

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ABSTRACT

Adhesive are indispensable component in wood composite which is directly affect its physical, mechanical and chemical properties which are classified into two categories as synthetic and natural adhesive. By experiencing the emission of formaldehyde vapors which are carcinogenic of synthetic based adhesive, the natural adhesives in market be competitive, however they were weak in bonding and water resistance. As to overcome the problem this study attempts to develop natural adhesive that contain environmental friendly material by using lignin and soy protein, study its bonding strength and water resistant ability by chemically modify the protein to make the composite boards can pass the physical and mechanical tests of the medium density fiberboard (MDF). Therefore, the modification of soy flour with different concentration of lignin had been formulated by adding other chemical such as sodium hydroxide as alkali solution to the formulation to reach the required properties of strength and water resistance. As s conclusion, from this study it was found that only internal bonding give the good result and can be acceptable. In addition, high bonding strength and good water resistance of adhesive can be achieved by some additional modification of soy protein and lignin.

PENGHASILAN BAHAN PELAKAT ASLI MENGGUNAKAN LIGNIN DAN PROTIN SOYA

ABSTRAK

Bahan pelekat adalah komponen utama dalam komposit kayu kerana ia mempengaruhi cirri-ciri fizikal, mekanikal dan kimia dan terbahagi kepada dua kategori iaitu pelekat sintetik dan pelekat asli. Akibat mengalami pengeluaran gas formaldehid yang karsinogenik daripada bahan pelekat sintetik, bahan pelekat asli akan competetif dalam pasaran, walaubagaimanapun pelekat asli lemah dalam ikatan serat dan sifat kalis air. Untuk menyelesaikan masalah tersebut, kajian ini bertujuan untuk menghasilkan bahan pelekat asli yang mengandungi bahan mesra alam dengan menggunakan lignin dan protin soya, mengkaji kekuatan ikatan dan kebolehan kalis air dengan mengubahsuai protin secara kimia untuk memastikan komposit kayu boleh melepasi ujian fizikal dan mekanikal bagi papan serat kepadatan sederhana (MDF). Oleh itu, pengubahsuaian serbuk soya bersama lignin berlainan kepekatan telah diformulakan dengan menambah beberapa bahan kimia seperti natrium hidroksida sebagai larutan alkali untuk menjadikan formulasi mencapai cirri-ciri diperlukan bagi kekuatan dan sifat kalis air. Kesimpulannya, daripada kajian ini, ia mendapati bahawa hanya ikatan dalaman MDF menunjukkan keputusan yang baikdan boleh diterima. Tambahan lagi, kekuatan ikatan MDF dan sifat kalis air bahan pelekat boleh dicapai dengan penambahan pengubahsuaian protin soya dan lignin.

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LIST OF SYMBOL/ABBREVIATION

A	Absorbance value
C	Concentration of lignin
cm	Centimeter
D	Absorbtivity
FTIR	Fourier Transform Infrared Spectroscopy
g	Gram
H	Hour
kg	Kilogram
L	Liter
m	Meter
mL	Milliliter
mm	Millimeter
MPa	Megapascal
mPA	MiliPascal
N	Newton
ºC	Degree Celsius
V_{MDF}	MDF volume
λ	Wavelength
ρ_{MDF}	MDF density

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In 2001, total sale of wood adhesive reach $ 6.1 billion as value the consumption of 13.3 million tones adhesive (Huang, 2007). Huang, 2007 also stated that adhesive are indispensable component in wood composite which is directly affect its physical, mechanical and chemical properties. Lei, 2009 also agreed with Huang by stated that wood adhesive play an important role in wood panel industry since the performance of the final wood panel depend on great degree of adhesive.

As the development of wood adhesive industry since 18th century, it can be classified into two categories which are adhesives from petrochemical and natural material (Huang, 2007). Nihat and Nilgül, 2002 stated that synthetic polymer resin based adhesive usually used in commercial wood composite product since it adhere well to wood and can form strong bond just like the wood. However, it is restricted because it is non-renewability and toxicity as well as highly cost since it was petroleum based product (Lei, 2009). Therefore, as a solution to the problem, natural adhesive being industrial interest lately since it was environmental friendly and ease to handle (Lei, 2009). Unfortunately, this type of adhesive is lack of bonding strength and almost no water resistance which mean it not a good adhesive to the wood or particle board.

1.2 Problem Statement

Formaldehyde based synthetic adhesive are restricted because it’s non-renewability and emission of formaldehyde vapors which are carcinogenic. However, recent natural adhesives in market were weak in bonding and water resistance.

In order to overcome the environmental issue of synthetic resin and weakness of bonding strength with water resistance issue, this study had came with the new formulation to develop natural adhesive using lignin and soy protein based on it various properties.

1.3 Research Objectives

The objectives of this study is to develop natural adhesive that contain environmental friendly material by using lignin and protein and study its bonding strength as well as the water resistant ability of the natural adhesive. Besides this research also attempt to chemically modify the protein to make the composite boards can pass the physical and mechanical tests of adhesive.

1.4 Scope of Study

1.5.1 To study the development of natural adhesive that contains environmental friendly material by using lignin and soy protein.

1.5.2 To analyze the properties of the natural adhesive in the bonding strength and water resistance ability of medium density fiberboard (MDF).

1.5 Significance of Study

The high demand in the wood industrialized world had caused pollution problem due to the widespread use of formaldehyde in synthetic resins adhesive which based on petrochemical. Therefore, it increasingly necessary to develop the natural adhesive with smaller environment impact which only used environmental friendly or non toxic material. The natural adhesive must be technically economically competitive, environmental acceptable, readily available and able to fully function as good adhesive which be the aim of this research. Natural adhesive also will be non-toxicity to human as well as environmental friendly.

1.6 Overview of the Thesis

As a conclusion, this study can improves the development of adhesive in wood composite industry which is more environmental friendly and give low cost of raw material (non petrochemical). For the next chapter, there will be the review of previous study about natural adhesive, deep review about lignin based adhesive and protein based adhesive as well as their properties. In third chapter, there will be the detail of the method that will be used in the development of natural adhesive using lignin and soy protein as well as the analysis to study its properties.

CHAPTER 2

LITERATURE REVIEW

This chapter consists of three subtopics that discuss about the previous study related to the developing natural adhesive using lignin and protein which are historical background of natural adhesive, development and properties of lignin based adhesive as well as development and properties of protein based adhesive.

2.1 Historical background of Natural Adhesive

A substance capable to hold material together by surfacing attachment was a definition of an adhesive by a dictionary stated by Nicholson (1991). Sun, Wang, Zhong & Yang (2008) estimated that, the demand of adhesive in US will reach 15.2 billion pound in 2004 and most of these adhesive are from petroleum resources. In contrast, Frihart (2005) stated that protein glues have been used for thousand years as common bio-based adhesive and many early civilizations learned to make adhesive from plants and animals but today most of bio-diesel been replace by synthetic adhesive . Therefore, Lei (2009) had made a conclusion that the development of wood adhesive divided into two stages which were natural adhesive as the first stages and be replaced by synthetic thermosetting resin as the second stage in order to overcome the deficiency of natural adhesive in water resistance and bonding strength.

However, industrial interest lately was switched to natural adhesive due to the limited sources of petrochemical and environmental issue of toxicity emission as well as the availability of natural material as waste from other industry such as lignin and protein. In addition, Sun et al. (2008) stated that natural or environmentally friendly adhesive got lots of concerns recently since there were limited petroleum resources, environmental pollution issue and health problem cause by petroleum based adhesive. However, as to overcome the environment pressure, several investigation and research had been made in order to upgrade the weakness of most natural adhesive (Lei, 2009). Lei (2009) also stated that, those natural adhesive can be modified or cross-linked using formulation that not contain any toxicity material but still can improve the adhesive performance. Huang (2007) had been give similar opinion as Lei (2009), which stated that an urgent need to develop environmentally friendly wood adhesive to solve hazardous issue associated with formaldehyde based adhesive since formaldehyde emission will give health problem.

Frihart (2005) stated that many sources of protein adhesive such as animal bones and hides, milk (casein), blood, fish skin and soybean have been used as the raw material. Besides that, tree and bushes also provide several adhesive materials which include pitch, tannins and lignin (Frihart, 2005). Although carbohydrates not found much in wood industry adhesive, but usually starch used in many packaging application as adhesive (Frihart, 2005). Most of these materials usually can be found as the waste product in different industry such as animal blood from slaughterhouse, besides, those materials have renewability properties.

2.2 Development and Properties of Lignin Based Adhesive

As lignin were different type of waste and abundance product from pulp mills, the material could be other option for the preparation of adhesive as the natural material as an alternative to replace formaldehyde based adhesive (Lei, 2009). Nihat & Nilgül (2002) also stated that lignin is one most abundant, renewable natural product on earth as a by-product of the pulping process. Hüttermann, Mai & Kharazipour (2001) also introduce that the pulp and paper industry produce technical lignin as by-product in large quantities about 30-50 million ton per year. Other than that, lignin also the most important natural product coming from plants (Lei, 2009). Lignin is important factor for structural integrity for the cell wall and stiffness as well as strength of the stem (Boerjan, Ralph & Baucher, 2003). Boerjan et al. (2003) also stated that lignin are complex racemic aromatic heteropolymers derived mainly from three hydroxycinnamyl alcohol monomers differing in their degree of methoxylation, p-coumaryl, coniferyl and sinapyl alcohol. In the other hand, Lei (2009) stated that in lignin natural form there is three dimensional polymers constituted of random polymerization of phenylpropane unit by ester and C-C bond.

Basically, lignin present in plant is quite variable and range about 20% to 40%. As lignin produce from pulping process (byproduct), the chemical pulping can be grouped into two classes which are sulfite and alkaline pulping (Lei, 2009). In sulfite pulping, the lignin fragment were called lignosulfate and give the lignin surface active, binding properties as well as hygroscopicity which lead to poor ability to co-crosslink with adhesive (Lei, 2009). Besides that, alkaline pulping was done with sodium hydroxide which third of it can be replace sodium sulfide and soda pulping as variation by adding catalytic quantities of anthraquinone (Lei, 2009). During the process, lignin extensively modified and cleavage of alkylaryl ether lingkage which drive the lignin fragment undergo condensation reaction (Lei, 2009). In the other hand, for the process of recovered sugar cane bagasse lignin, acidification of a black liquor produce by soda delignification of steam exploded sugar cane bagasse. However, this process produce low molecular weight lignin fragment (Guerra, Ferraz, Cotrim & Silva, 2000). In addition, Bourbonnais, Paice, Reid, Lantheir & Yaguchi (1995) found that kraft pulping delignified by combination of laccase and 3-ethylbenzthiazoline-6-sulfonate and it was reported that were more than 50% delignification of kraft pulp with laccase and another moderator or by repeated treatment following by alkaline extraction.

2.2.1 Chemical modification of lignin

Although, lignin present in plant act together with hemicelluloses as a perfect natural adhesive for cellulose fibers, isolated technical lignin generally are poor binders for wood composites compared to synthetics resins (Frihart, 2010). Frihart (2010) also stated that lignosulfonates were the most used technical lignin for making lignin-based adhesive, however in most cases they were isolated, purified and modified before used for producing adhesive since the required high pressure and temperature for resin curing. Frihart (2005) had stated that both tannin and lignin as adhesive tend to have good moisture resistance and are not readily attacked by microorganisms.

Mansouri, Pizzi and Salvadó (2007) found the following:

> *Lignin based wood adhesives prepared without formaldehyde substituted by non-volatile non-toxic aldehyde, namely glyoxal, were prepared and tested for application to wood panels such as particleboard. The adhesives not only yielded good internal bonding strength results of the board to comfortably pass relevant international standard specifications, but also showed sufficient reactivity to yield panels in press times comparable to those of formaldehyde-based commercial adhesive.* (p. 6)

Lei (2009) found that glyoxalated lignin gave low wood joint strength and cannot be used alone as wood adhesive until it be cross-linked furtherly. He also stated that, the addition of 4,4-diphenylmethane diisocyanate (pMDI) gave improvement of the MOE on curing joint. Therefore, it can be conclude that improvement of lignin can be made by reaction with the glyoxal and addition of pMDI.

2.3 Development and Properties of Protein Based Adhesive

Protein had been used for long as wood adhesive and can be divided into two groups: one is based on plant protein adhesive; the other is based animal protein adhesive (Lei, 2009). Frihart (2005) stated that many sources have been used for protein based adhesive, including animal bones and hide, milk (casein), blood, fish skins and soybeans. As most other biomass material, protein also not uniform in composition and the process for using different sources of protein to make adhesives are varies (Frihart, 2005). In order to make a useful adhesive, the raw protein must be denatured to expose the polar group for solubilization and bonding purpose (Frihart, 2005).

Huang (2007) stated that, animal bones and hide contain high amount of amide group, free amino groups and carboxylic acid group which interact with the protein chains thus, provide the strength as adhesive toward the wood. This type of adhesive widely used in furniture, unfortunately, their many undesirable properties such as low moisture resistance, relatively high price and susceptibility to biological degradation make they had been replace by synthetic resins (Huang, 2007). In addition, Huang (2007) also found that blood based adhesive can be improved by addition of formaldehyde and phenol formaldehyde resin in their properties of water resistance, strength and mold resistance. Frihart (2005) also stated that blood protein from beef and hogs gave more water resistance than others protein, however the availability for industrialize scale as well as composition were not consistent. Therefore, soy protein which have low cost, large supply, consistent composition as soybean flour and other special properties (Frihart, 2005) make most of the present research that work on protein adhesive was concentrate on soy protein and had been proposed industrially (Lei, 2009).

2.3.1 Soy protein based adhesive

Soy protein contains about 20% oil, 34% carbohydrates 40% protein and 4.9% ash (Huang, 2007). However, Lei (2009) stated that soy based protein contains 40-60% protein formerly and more that 90% were later. Huang (2007) also found that soy oil composed of saturated and unsaturated triglyceride, soybean carbohydrates consist polysaccharides such as cellulose, hemicelluloses and pectin, and another 18 amino acid in soy protein.

Huang (2007) stated that major commercial soybean product includes soy flour, soybean oil, defatted soybean meal, soy protein concentrate (SPC) and soy protein isolate (SPI). All of the products produced through several processes from soybean powder. By removing soybean oil, defatted soybean meal and soy flour can be produce. Then, from defatted soy meal soy protein concentrate (SPC) and soy protein isolate (SPI) achieved. Table 2.1 shows the composition of different soy protein product.

Soy based adhesive were first developed around 1923 (Sun et. al., 2008). Huang (2007) also stated that soy based adhesive widely used in the production of wood composites since 1930s until 1960s. Unfortunately, as its poor water resistance, weak bonding strength and poor bio degradation resistance (Lei, 2009) as well as low gluing strength (Sun et al., 2008) make it been replace by synthetic resin. However, lots of research and investigation about this problem had been made to improve those properties since soybean is abundant, inexpensive, renewable and sustainable as well as environmental friendly.

Table 2.1: The composition of different soy protein products

g/100g product	Soy flour	Soy protein concentrate (SPC)	Soy protein isolate (SPI)
Protein	48	64	92
Fat	0.3	0.3	0.5
Moisture	10	10	<5
Fibers	3.0	4.5	<1
Ash	7	7	4
Carbohydrate	31-32	14-15	-

Source: Huang (2007)

2.3.1.1 Modification of soy protein

Because of the inferior properties of soy protein based adhesive, various new method have been investigated in order to improve the strength and water resistance wood composite by soy based adhesive (Huang, 2007). Lei (2009) stated that recently, soy protein been modified and combined with urea formaldehyde (UF), phenol formaldehyde (PF), isocynates or others to obtain more water resistance adhesive as well as stronger bonding. Unfortunately, those approaches contain high amount of synthetic material and maximization of natural component in the wood adhesive is demand (Lei, 2009). Soy protein can be chemically, physically or enzymatically modified in order to achieve desired properties of natural adhesive including hydrolysis, cleavage of disulphide bond, crosslinking, acylation, oxidation, reaction with alkoxy silane and copolymerization (Lei, 2009).

Huang (2007) had stated that soy flour (SF), maleic anhydride (MA), sodium hydroxide (NaOH) and polyethylenimine (PEI) can be combine as adhesive and superior to alkali-modified in term of enhancing strength and water resistance of particleboard. Huang (2007) also stated that by using curing agent such as sulfur containing compound, epoxy compound and aldehydes for cross linking of soy protein, will improve the strength and water resistance of soy based adhesive. As a conclusion, the soy protein needs to be modified by alkylation and adding of suitable curing agent in order to optimum strength and water resistance. Figure 2.1 illustrate the structure of denaturized soy protein.

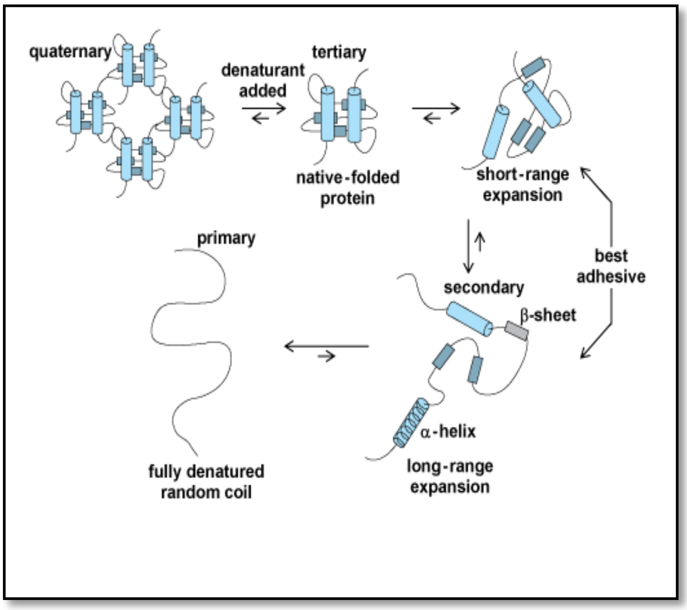

Figure 2.1: An illustration of the structure of protein chain during denaturized

Source: Frihart (2010)

"*Alkali-modified soy protein adhesive was reported to be stronger and more water resistant compared with adhesive containing unmodified soy protein*." (Lei, 2009, pg 22). In the other hand, Sun et al. (2008) support modified soy protein adhesive gave more strength and water resistance compared to unmodified by experimenting several procedures of modification of soy protein in their research.

2.4 Wood-based Composite

Wood-based composite is terms present a group of product from wood material which was adhesively bonding together (Stark, Cai & Carll 2010). Table 2.2 indicates the classification of wood-based composite which reflect the latest product development.

Table 2.2: Classification of wood-based composites

Veneer-based material
Plywood
Laminated veneer lumber (LVL)
Parallel-strand lumber (PSL)
Laminates
Glue-laminated timbers
Overlayed materials
Laminated wood–nonwood composites[b]
Multiwood composites (COM-PLY[c])
Composite material
Fiberboard (low-, medium-, or high-density)
Cellulosic fiberboard
Hardboard
Particleboard
Waferboard
Flakeboard
Oriented strandboard (OSB)
Laminated strand lumber (LSL)
Oriented strand lumber (OSL)
Wood–nonwood composites
Wood fiber–polymer composites
Inorganic-bonded composites

Source: Maloney (1986)